

AD-A197 177

## REPORT DOCUMENTATION PAGE

Unclassified		1b RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Distribution-unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 28		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Rutgers, The State University of New Jersey	6b. OFFICE SYMBOL (If applicable) 4B883	7a. NAME OF MONITORING ORGANIZATION Electrochemical Sciences Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) P.O. Box 939 Piscataway, NJ 08854		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy St. Arlington, VA 22217-5000	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable) 1113ES	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy St. Arlington, VA 22217-5000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO N00014	PROJECT NO 413d008
		WORK UNIT ACCESSION NO	
11. TITLE (Include Security Classification) New Rhenium Chalcogenides with Isolated $[\text{Re}_6\text{X}_8]$ -Cluster Units: Preparation & Properties			
12. PERSONAL AUTHOR(S) G. Huan, M. Greaney, and M. Greenblatt			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 7/1/87 TO 7/15/88	14. DATE OF REPORT (Year, Month, Day) July 15, 1988	15. PAGE COUNT 8
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>New ternary rhenium chalcogenides <math>\text{A}_4\text{Re}_6\text{X}_{12}</math> with A = Tl, Cu, Na, Cs, and X = Se; A = Tl, Rb and X = S; <math>\text{A}_2\text{Re}_6\text{X}_{12}</math> with A = Pb and X = S, Se have been prepared by high temperature and ion exchange techniques in closed systems. X-ray diffraction powder patterns show them to be isostructural with previously reported <math>\text{A}_4\text{Re}_6\text{X}_{12}</math> which are characterized by <math>\text{Re}_6\text{X}_8</math> cluster units interconnected into a three-dimensional network structure by X and <math>\text{X}_2</math> linkages. Temperature variation of resistivity measured on sintered pellets shows semiconducting behavior in agreement with 24 electrons per cluster filling the bonding valence band which is separated in energy from the empty antibonding conduction band. Variation of the number and size of the A and X ions are correlated with structural stability in these compounds.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Martha Greenblatt		22b. TELEPHONE (Include Area Code) (201) 932-3277	22c. OFFICE SYMBOL

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NEW TERNARY RHENIUM CHALCOGENIDES WITH ISOLATED  $[\text{Re}_6\text{X}_8]$ -CLUSTER UNITS:  
PREPARATION AND PROPERTIES.

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DTIC TAB		<input checked="" type="checkbox"/>
Unannounced		<input type="checkbox"/>
Justification		<input type="checkbox"/>
By _____		
Distribution/ _____		
Availability Codes		
Dist	Avail and/or Special	
A-1		

ABSTRACT

New ternary rhenium chalcogenides  $\text{A}_4\text{Re}_6\text{X}_{12}$  with  $\text{A} = \text{Tl}, \text{Cu}, \text{Na}, \text{Cs}$ , and  $\text{X} = \text{Se}$ ;  $\text{A} = \text{Tl}, \text{Rb}$  and  $\text{X} = \text{S}$ ;  $\text{A}_2\text{Re}_6\text{X}_{12}$  with  $\text{A} = \text{Pb}$  and  $\text{X} = \text{S}, \text{Se}$  have been prepared by high temperature and ion exchange techniques in closed systems. X-ray diffraction powder patterns show them to be isostructural with previously reported  $\text{A}_4\text{Re}_5\text{X}_{12}$  which are characterized by  $\text{Re}_6\text{X}_8$  cluster units interconnected into a three-dimensional network structure by X and  $\text{X}_2$  linkages. Temperature variation of resistivity measured on sintered pellets shows semiconducting behavior in agreement with 24 electrons per cluster filling the bonding valence band which is separated in energy from the empty antibonding conduction band. Variation of the number and size of the A and X ions are correlated with structural stability in these compounds.

MATERIALS INDEX: ternary rhenium chalcogenides,  $\text{Re}_6\text{X}_8$  clusters, synthesis, semiconducting.

Introduction

Clustering is a common phenomenon for transition metal compounds, which often leads to low dimensionality and interesting physical properties including metallic behavior, charge-density wave (CDW) instability and superconductivity.

Four types of clustering have been found in rhenium compounds: (a)  $\text{Re}_2$  units as in  $\text{ReCl}_4$  (1) and  $\text{ReP}_4$  (2); (b)  $\text{Re}_3$  units as in  $\text{Re}_3\text{Cl}_9$  (3); (c)  $\text{Re}_4$  units as in  $\text{Re}_{12}\text{P}_{26}$  (4) and (d)  $\text{Re}_6$  units as in the  $[\text{Re}_6\text{X}_8]$ -cluster chalcogenides (5-12). Although a huge amount of work has been reported on molybdenum chalcogenides with  $\text{Mo}_6$  cluster units and their condensed analogs, considerably fewer reports appeared to date, on ternary rhenium chalcogenides with  $\text{Re}_6$  units.

The earliest work on Re analogs of  $\text{Mo}_6\text{S}_8$ , the so-called Chevrel phases, were published by M. Spangenberg and W. Bronger in 1978 (5,6). They prepared  $\text{Na}_4\text{Re}_6\text{S}_{12}$ ,  $\text{K}_4\text{Re}_6\text{S}_{12}$  and  $\text{Cs}_4\text{Re}_6\text{S}_{13}$ . The structure of these ternary sulfides is characterized by  $\text{Re}_6$  units arranged in an almost regular octahedron with average Re-Re distances of 2.61 Å (~2.75 Å in Re metal). Eight S atoms are arranged over the rhenium octahedron surfaces forming  $\text{Re}_6\text{X}_8$  clusters as structural building blocks. S or  $\text{S}_2$  groups couple the  $[\text{Re}_6\text{S}_8]$  units three-dimensionally (3D) via Re atoms. The alkali atoms are located in the interstices of these skeletal structures (5,6).

These results were confirmed by S. Chen and W.R. Robinson (7) who observed two different crystal forms in both the Na and K,  $\text{A}_4\text{Re}_6\text{S}_{12}$  compounds: a red insulating and a black semi-conducting phase, respectively. The red form slowly transforms to the black form upon exposure to  $\text{H}_2\text{O}$  or  $\text{Na}_2\text{S}$  or  $\text{HCl}$  or air (7).  $\text{A}_2\text{Re}_6\text{S}_{11}$  with A = Sr, Ba, Eu, and  $\text{Li}_4\text{Re}_6\text{S}_{11}$  reported by Bronger et al (8,9,10) show structural features which are nearly identical to the alkali metal compounds described above with the alkali earth metals (or Eu, or Li) occupying cavities created by the 3D network of sulfur linked  $\text{Re}_6\text{S}_8$  units. The diamagnetic behavior of these phases suggest 24 electrons per cluster unit corresponding to a filled band.

More recently, the new phases  $\text{Rb}_4\text{Re}_6\text{S}_{13}$ ,  $\text{Rb}_2\text{K}_2\text{Re}_6\text{S}_{13}$ ,  $\text{Cs}_4\text{Re}_6\text{S}_{13}$ ,  $\text{Rb}_4\text{Re}_6\text{Se}_{12}$ ,  $\text{K}_4\text{Re}_6\text{Se}_{12}$  and  $\text{Cs}_4\text{Re}_6\text{S}_{9.45}\text{Se}_{3.55}$  were synthesized (11). The only ternary rhenium telluride  $\text{Li}_{15}\text{Re}_6\text{Te}_{15}$  was prepared by lithium intercalation of  $\text{Re}_6\text{Te}_{15}$  ( $([\text{Re}_6\text{Te}_8]\text{Te}_6)\text{Te}$ ) (12). However, this compound has not been characterized adequately, and it is doubtful that such a large number of electrons per formula unit can be accepted by the host compound. The known ternary  $\text{Re}_6\text{X}_8$ -cluster compounds are summarized in Table I.

TABLE I. Three Types of Known Ternary Rhenium Chalcogenides

$\text{A}_4/\text{A}_2^{1/2}\text{Re}_6\text{X}_{11}$		$\text{A}_4\text{Re}_6\text{X}_{12}$		$\text{A}_4\text{Re}_6\text{X}_{13}$	
Composition	Space Group	Composition	Space Group	Composition	Space Group
$\text{Li}_4\text{Re}_6\text{S}_{11}$	Pccn	$\text{Na}_4\text{Re}_6\text{S}_{12}$	C2/c	$\text{K}_2\text{Rb}_2\text{Re}_6\text{S}_{13}$	C2/c
$\text{Sr}_2\text{Re}_6\text{S}_{11}$	C2/c	$\text{K}_4\text{Re}_6\text{S}_{12}$	C2/c	$\text{Rb}_4\text{Re}_6\text{S}_{13}$	C2/c
$\text{Ba}_2\text{Re}_6\text{S}_{11}$	C2/c	$\text{K}_4\text{Re}_6\text{Se}_{12}$	C2/c	$\text{Cs}_4\text{Re}_6\text{S}_{13}$	P2 <sub>1</sub> /n
$\text{Eu}_2\text{Re}_6\text{S}_{11}$	R3c	$\text{Rb}_4\text{Re}_6\text{Se}_{12}$	C2/c	$\text{Cs}_4\text{Re}_6\text{S}_{9.45}\text{Se}_{3.55}$	C2/c
				$\text{Cs}_4\text{Re}_6\text{Se}_{13}$	C2/c

In this paper we report on the syntheses, chemical and electric transport properties of a number of new ternary rhenium chalcogenides  $\text{A}_4\text{Re}_6\text{X}_{12}$  with A = Tl, Cu, Na, Cs, X = Se; A = Tl, Rb, X = S, and  $\text{A}_2\text{Re}_6\text{X}_{12}$  with A = Pb, X = S, Se.

### Experimental

$\text{Tl}_4\text{Re}_6\text{S}_{12}$  and  $\text{Tl}_4\text{Re}_6\text{Se}_{12}$  were prepared by heating stoichiometric  $\text{TlX}$  (X = S, Se), Re metal and X in evacuated quartz tubes at ~1000°C for a week and slowly cooling down to room temperature over a period of two weeks.  $\text{A}_4\text{Re}_6\text{X}_{12}$  (A = Na, K; X = S, Se) were prepared either directly from the corresponding elements using the same procedure as above, or by replacement of Tl in  $\text{Tl}_4\text{Re}_6\text{X}_{12}$  by ion

exchange method. All the other phases reported here were obtained by ion exchange method (13).

Phases were identified by powder X-ray diffraction using graphite monochromatized  $\text{CuK}\alpha$  radiation with a computer controlled Scintag PAD IV diffractometer. Unit cell parameters were determined by fitting the observed X-ray powder pattern by a least square program. The X-ray line position of the samples were corrected by using Si as an internal standard. Chemical analysis was carried out by a dc-plasma emission spectrometer. Temperature variation of the resistivity of sintered pellets was measured using the Van der Pauw technique (14) in a conventional cryostat.

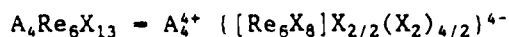
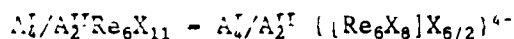
### Results and Discussion

The thallium compounds,  $\text{Tl}_4\text{Re}_6\text{X}_{12}$  with  $\text{X} = \text{S}, \text{Se}$  form as grey polycrystalline materials with metallic luster. Single crystal growth, structure determination and physical property measurements will be reported in a separate paper (15). Products of the ion exchange procedure appear in grey powder form. All phases prepared are stable in air and can only be dissolved in oxidizing acids. The Tl ions located in interstitial positions are highly mobile as evidenced by their partial removal upon treatment with  $\text{I}_2/\text{CH}_3\text{CN}$  solution at room temperature. The low limit of  $x$  in  $\text{Tl}_x\text{Re}_6\text{Se}_{12}$  was found to be  $\sim 1.8$ . Further deintercalation results in broadening of the X-ray reflection peaks and finally decomposition.

All the phases formed may be indexed based on space group  $\text{C2/c}$ . Cell parameters of the compounds prepared in this work along with those of previously reported  $\text{A}_4\text{Re}_6\text{X}_{12}$  (5,6,11) phases given for comparison are listed in Table II. The X-ray powder patterns of selected phases are given in Table III.

Fig. 1 shows the variation of cell volumes with effective ionic radii of the ternary elements. The cell volume ( $V$ ) increases almost linearly with ionic radius ( $r$ ) when  $\text{A} = \text{alkali metals}$  or  $\text{A} = \text{Cu, Pb, and Tl}$ , respectively. The slopes of the  $V$  vs.  $r$  lines are almost the same. Apparently, the alkali metal rhenium chalcogenides have larger cell volumes than other corresponding ternary rhenium chalcogenides with comparable A ionic radius; for example,  $r_{\text{K}^+} < r_{\text{Tl}^+}$  but the volume of  $\text{K}_4\text{Re}_6\text{X}_{12}$  is larger than that of  $\text{Tl}_4\text{Re}_6\text{X}_{12}$  (Table II). This can be attributed to the fact that  $\text{Tl}^+$  is more polarizing than  $\text{K}^+$  which leads to more covalent Tl-X bonds. This argument may be applied for  $\text{Cu}^+$  and  $\text{Pb}^{2+}$  as well. Furthermore, the  $a$  cell parameter increases considerably with increasing effective ionic radii while the  $b$  and  $c$  dimensions change only a small amount (Table II). For  $\text{A}_4\text{Re}_6\text{Se}_{12}$  ( $\text{A} = \text{K, Rb and Cs}$ ),  $b$  is constant. This may be explained by the fact that the  $\text{Se}_2$  bridging groups located along the  $a$  direction (5,6) are expected to be more flexible than the Se bridging atoms occurring along  $b$  and  $c$ .

As discussed above and evident in Table I, there are three different types of ternary rhenium chalcogenides reported so far:



The basic structural features are essentially the same -  $\text{Re}_6\text{X}_8$  cluster units -

TABLE 11. Cell Constants of Some New  $A_4^I/A_2^I\text{Re}_6\text{X}_{12}$  Phases

Compound	Prep. Method	a (Å)	b (Å)	c (Å)	$\beta$ (°)	V (Å <sup>3</sup> )	Remark
$\text{TL}_4\text{Re}_6\text{Se}_{12}$	H.S.	17.205 (2)	9.865 (2)	12.206 (2)	90.72 (2)	2071.7 (4)	This work
$\text{Na}_4\text{Re}_6\text{Se}_{12}$	H.S.	16.424 (5)	9.864 (3)	11.823 (3)	91.67 (3)	1925.9 (9)	This work
$\text{K}_4\text{Re}_6\text{Se}_{12}$	H.S.	17.195 (8)	10.020 (7)	12.286 (8)	91.35 (5)	2116.3 (12)	This work
$\text{K}_4\text{Re}_6\text{Se}_{12}$	$\text{K}_2\text{CO}_3 + \text{Re}$ + Se	17.167 (5)	10.029 (7)	12.293 (1)	91.37 (6)	2115.9	(11)
$\text{Rh}_4\text{Re}_6\text{Se}_{12}$	I.E.	17.509 (8)	10.020 (3)	12.352 (5)	90.67 (4)	2166.8 (10)	This work
$\text{Rh}_4\text{Re}_6\text{Se}_{12}$	$\text{Rh}_2\text{CO}_3 + \text{Re}$ + Se	17.487 (8)	10.024 (1)	12.350 (1)	90.59 (6)	2164.7	(11)
$\text{Cs}_4\text{Re}_6\text{Se}_{12}$	I.E.	18.078 (7)	10.019 (3)	12.430 (6)	91.51 (4)	2250.5 (9)	This work
$\text{Cu}_4\text{Re}_6\text{Se}_{12}$	I.E.	17.141 (6)	9.857 (7)	10.288 (6)	90.41 (5)	1738.1 (10)	This work
$\text{Pb}_2\text{Re}_6\text{Se}_{12}$	I.E.	16.544 (7)	9.741 (4)	12.041 (8)	90.52 (5)	1940.4 (12)	This work
$\text{TL}_4\text{Re}_6\text{S}_{12}$	H.S.	16.632 (2)	9.586 (1)	11.786 (2)	90.59 (1)	1879.0 (3)	This work
$\text{Na}_4\text{Re}_6\text{S}_{12}$	H.S.	15.843 (5)	9.576 (3)	11.492 (4)	92.46 (3)	1741.8 (7)	This work
$\text{Na}_4\text{Re}_6\text{S}_{12}$	$\text{Na}_2\text{CO}_3 + \text{Re}$ + $\text{H}_2\text{S}$ .	15.830 (8)	9.582 (4)	11.472 (6)	92.41 (4)	1738.6	(5,6)
$\text{K}_4\text{Re}_6\text{S}_{12}$	H.S.	16.480 (6)	9.679 (4)	11.816 (6)	91.13 (4)	1884.3 (1)	This work
$\text{K}_4\text{Re}_6\text{S}_{12}$	$\text{K}_2\text{CO}_3 + \text{Re}$ + $\text{H}_2\text{S}$ .	16.490 (9)	9.670 (6)	11.828 (7)	91.01 (4)	1885.8	(5,6)
$\text{Rh}_4\text{Re}_6\text{S}_{12}$	I.E.	16.829 (4)	9.745 (3)	11.948 (2)	91.08 (2)	1963.0 (5)	This work
$\text{Pb}_2\text{Re}_6\text{S}_{12}$	I.E.	15.845 (10)	9.602 (9)	11.527 (8)	92.19 (8)	1752.5 (15)	This work

Note: H.S. High temperature synthesis  
I.E. Ion exchange method

Table III: X-Ray Powder Diffraction Data for Selected  $A_4\text{Re}_5X_{12}$  Phases

$\text{Ti}_4\text{Re}_5\text{S}_{12}$				$\text{Ti}_4\text{Re}_5\text{Se}_{12}$				$\text{Na}_4\text{Re}_5\text{Se}_{12}$			
hkl	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	I/I <sub>0</sub>	hkl	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	I/I <sub>0</sub>	hkl	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	I/I <sub>0</sub>
200	8.29	8.32	86	200	8.58	8.60	79	200	8.22	8.21	100
$\bar{1}11$	6.79	6.81	100	$\bar{1}11$	7.01	7.03	100	$\bar{1}11$	6.96	6.94	34
002	5.89	5.89	19	002	6.10	6.10	20	111	6.85	6.84	88
020	4.79	4.79	26	202	4.94	4.95	15	002	5.95	5.94	12
311	4.43	4.43	34	311	4.58	4.58	28	020	4.93	4.93	3
$\bar{2}21$	3.922	3.923	15	221	4.04	4.03	7	112	4.82	4.83	3
$\bar{1}13$	3.557	3.558	20	$\bar{1}13$	3.682	3.683	14	220	4.24	4.23	3
$\bar{4}02$	3.413	3.412	16	$\bar{4}02$	3.535	3.536	10	$\bar{1}31$	3.113	3.116	3
402	3.382	3.381	18	$\bar{2}22$	3.513	3.514	7	$\bar{4}21$	3.063	3.066	3
$\bar{4}20$	3.141	3.141	10	222	3.492	3.493	13	313	3.013	3.015	2
$\bar{1}31$	3.033	3.034	30	$\bar{4}20$	3.242	3.242	13	223	2.870	2.870	3
223	2.846	2.847	28	$\bar{1}31$	3.124	3.124	20	$\bar{1}32$	2.839	2.840	4
132	2.771	2.772	67	004	3.053	3.051	8	$\bar{2}04$	2.820	2.821	6
331	2.692	2.693	12	$\bar{2}23$	2.957	2.958	16	$\bar{5}12$	2.793	2.791	4
024	2.510	2.510	18	223	2.938	2.939	10	204	2.770	2.769	5
332	2.501	2.501	22	114	2.869	2.869	51	$\bar{3}31$	2.750	2.749	19
$\bar{1}33$	2.455	2.454	24	331	2.774	2.774	24	024	2.546	2.546	4
$\bar{4}04$	2.416	2.416	13	$\bar{6}02$	2.608	2.608	10	332	2.530	2.532	8
224	2.398	2.397	10	314	2.585	2.586	35	602	2.460	2.458	3
041	2.348	2.348	26	$\bar{1}33$	2.532	2.533	11	$\bar{4}04$	2.439	2.441	3
$\bar{3}33$	2.269	2.268	67	$\bar{4}04$	2.504	2.504	16	404	2.374	2.374	9
242	2.142	2.143	29	621	2.425	2.424	12	$\bar{5}31$	2.290	2.289	15
$\bar{3}15$	2.123	2.123	14	710	2.385	2.385	11	531	2.270	2.271	7
043	2.046	2.046	13	$\bar{3}33$	2.343	2.343	72	622	2.201	2.200	5
334	2.013	2.012	11	$\bar{6}22$	2.305	2.305	17	315	2.107	2.108	28
$\bar{2}43$	1.990	1.989	14	$\bar{4}24$	2.232	2.232	12	441	2.077	2.076	5
730	1.907	1.907	21	$\bar{2}42$	2.213	2.213	12	334	2.062	2.061	4
$\bar{8}21$	1.886	1.886	27	$\bar{3}15$	2.200	2.200	10	$\bar{2}43$	2.035	2.034	7
425	1.878	1.878	38	315	2.181	2.181	7	442	1.99	2.001	5
$\bar{8}22$	1.820	1.820	25	$\bar{4}41$	2.110	2.110	13	604	1.985	1.984	3
$\bar{1}52$	1.813	1.813	15	334	2.078	2.078	7	$\bar{8}02$	1.956	1.957	4
351	1.790	1.790	13	$\bar{2}43$	2.052	2.052	15	802	1.922	1.923	7
$\bar{4}06$	1.783	1.783	20	730	1.970	1.969	15	135	1.908	1.908	4
823	1.709	1.709	10	$\bar{5}15$	1.963	1.963	10	$\bar{7}31$	1.892	1.892	8
136	1.664	1.664	34	$\bar{1}35$	1.950	1.950	29	$\bar{6}24$	1.887	1.887	3
$\bar{9}13$	1.654	1.654	16	821	1.942	1.942	39	$\bar{8}21$	1.879	1.879	3
				910	1.877	1.877	23	821	1.863	1.863	9
				$\bar{1}52$	1.867	1.867	25	910	1.794	1.794	4
				$\bar{4}06$	1.848	1.848	17	406	1.763	1.764	6
				$\bar{1}53$	1.767	1.767	9	444	1.711	1.711	5
				$\bar{4}44$	1.757	1.757	6	136	1.684	1.684	4
				136	1.719	1.720	7	061	1.629	1.629	5
				245	1.697	1.698	6				
				$\bar{9}31$	1.641	1.640	14				
				$\bar{8}41$	1.608	1.609	6				

Figure 1. Variation of the unit cell volumes as a function of the effective ionic radii of A cations in  $A_4Re_6X_{12}$  (dashed line, X = Se; solid line X = S)

in all. The primary difference between the three stoichiometries is the way the  $Re_6X_8$  units are linked in 3D. With increasing number of X per formula unit, the X bridging atoms are replaced stepwise by  $X_2$  bridging groups. The number of X and whether the compound is stable with X equal to S or Se, or both, actually depends on the size of A and the number of A per formula unit.  $X_2$  groups will provide more space than X and Se will provide more space than S. Thus, when A = Li, a small ion, only the sulfide exists and the number of S per formula is 11. Although Sr, Ba, and Eu are comparatively large, their number per formula is only 2, respectively, thus, the sulfides are stable. As the size of A increases, it requires more space, so either the number of X increases or the corresponding selenide becomes the more stable phase. It should be emphasized that this argument applies only for the thermodynamically most stable phases which were obtained in an open system with excess carbonates and  $H_2S$  (5-11). However, if the reaction is carried out in a closed system, the possibility for the formation of less stable or even metastable phases exists. This might be the reason for the isolation of the new phases reported in this work, even though some of the ternary elements might be much larger, or smaller than the "optimal" size required for the formation of the thermodynamically most stable structures.

Fig. 2 shows the results of selected resistivity measurements. All of the

(a)

(b)

Figure 2. Temperature dependence of the resistivity for selected  $A_4Re_6X_{12}$  phases: (a) dashed line  $Tl_4Re_6S_{12}$ ; solid line  $Cs_4Re_6Se_{12}$ ; (b)  $Tl_4Re_6Se_{12}$

phases investigated show semiconducting behavior, which is consistent with the assumption that there are 24 Re-Re orbitals per  $\text{Re}_6$  cluster unit of which 12 are bonding orbitals forming the valence band and 12 are antibonding orbitals forming the conduction band (16-19). Re is in the +3 formal oxidation state in these compounds (16). Thus, the 24 valence electrons available for each  $\text{Re}_6$  cluster fill the valence band, leaving the conduction band empty. Interesting questions to ask are: what is the actual valence of Re in these compounds? Is it possible to populate the antibonding orbitals (i.e. exceeding the magic number of  $24e^-/\text{unit}$ ) by appropriate chemical substitution, and if it is, what effects will that have on the electronic properties? Current work in progress in our laboratory is addressing some of these issues.

### Conclusion

We have prepared new ternary rhenium chalcogenides  $\text{A}_4\text{Re}_6\text{X}_{12}$  with A = Tl, Cu, Na, Cs and X = Se; A = Tl, Rb and X = S;  $\text{A}_2\text{Re}_6\text{X}_{12}$  with A = Pb and X = S, Se by high temperature and ion exchange methods in closed systems. X-ray powder diffraction shows that these phases are isostructural with  $\text{K}_4\text{Re}_6\text{S}_{12}$  which is characterized by isolated  $\text{Re}_6\text{X}_8$  cluster units interconnected by X and  $\text{X}_2$  bridging groups into a 3D network structure. The observed increase of the unit cell volume, with increasing effective ionic radii of the A cations which are located in the interstitial cavities of the 3D skeletal structure is not unexpected.

The temperature dependence of resistivity of the new ternary rhenium compounds indicates semiconducting behavior, consistent with 24 electrons per cluster completely filling the valence band.

### Acknowledgment

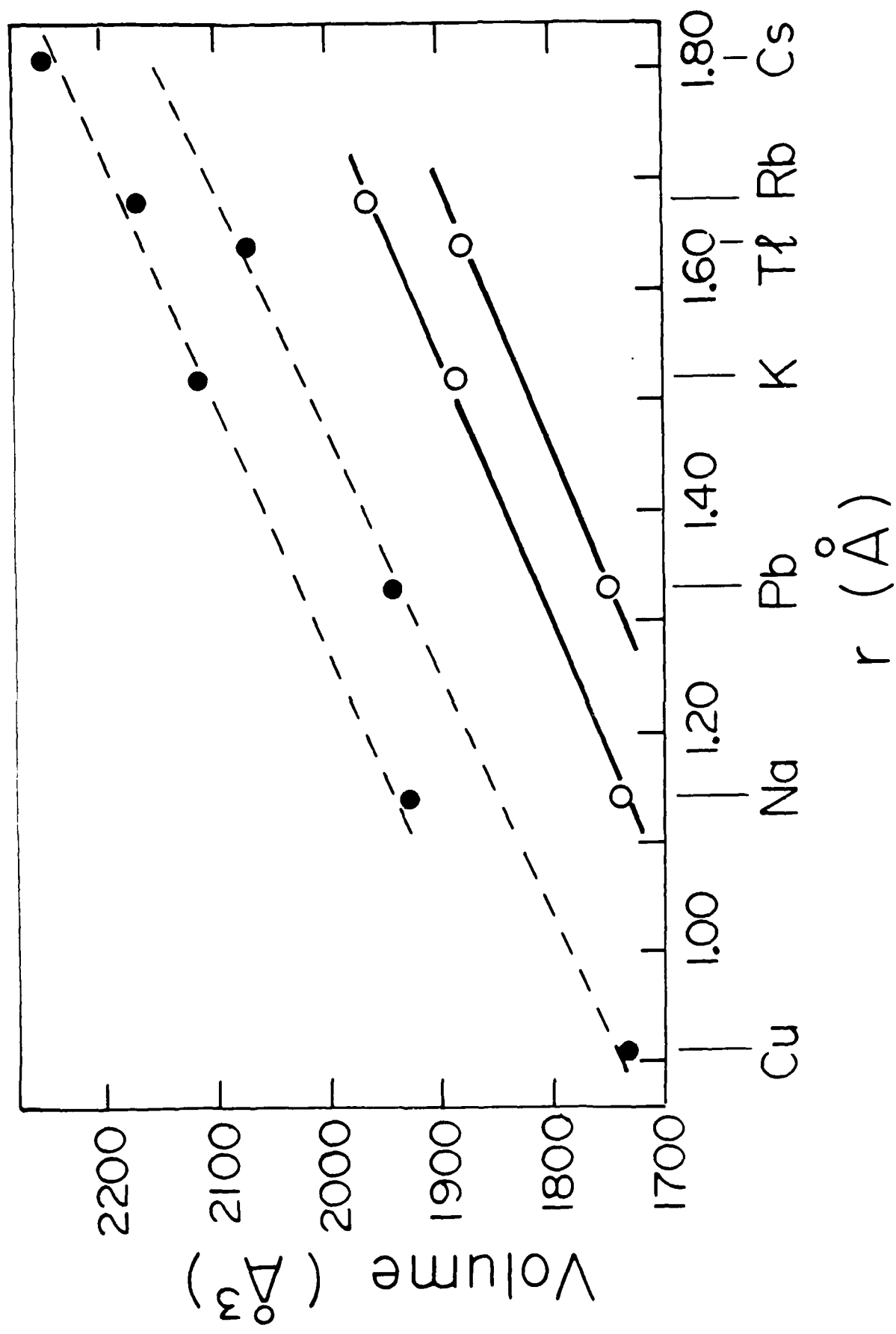
This research received partial support from the Office of Naval Research, the National Science Foundation - Solid State Chemistry Program, Grant DMR-84-04003 and DMR-87-14072

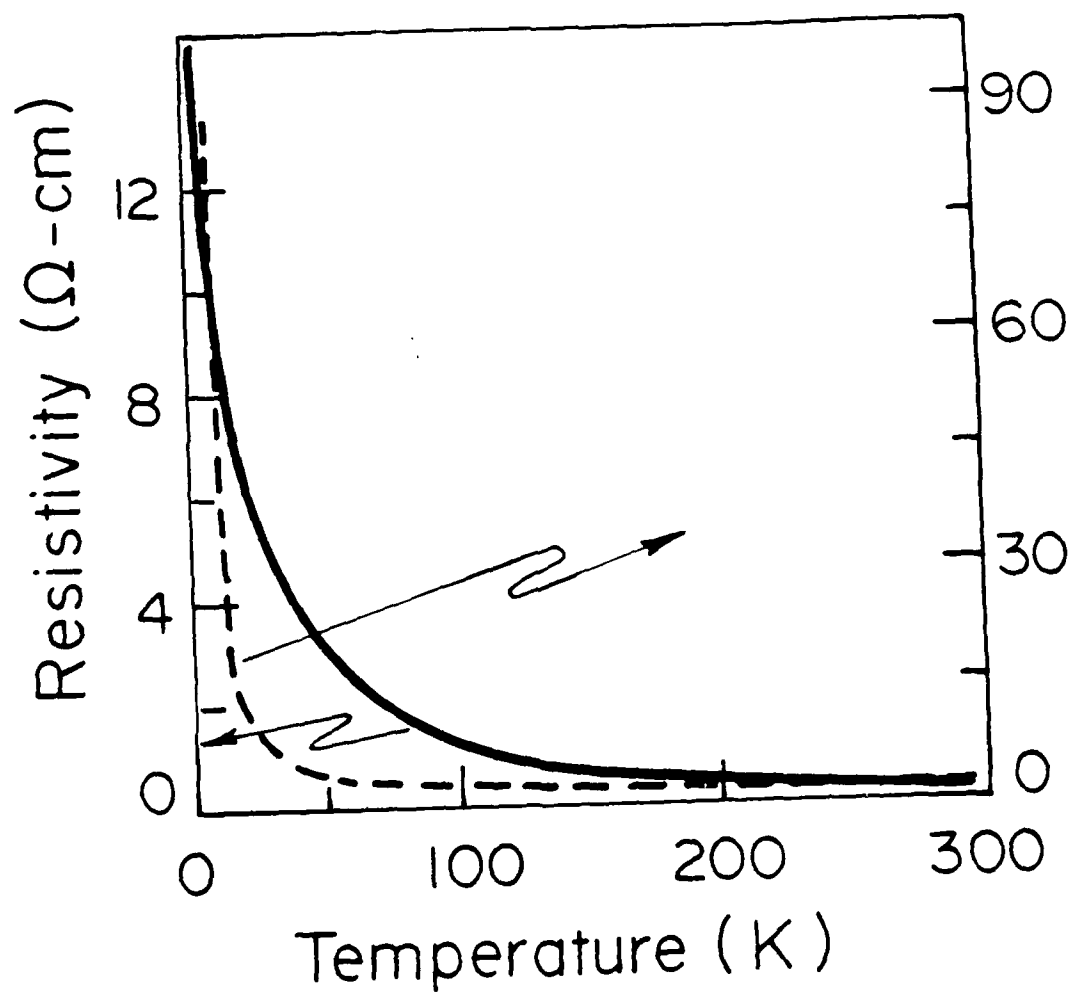
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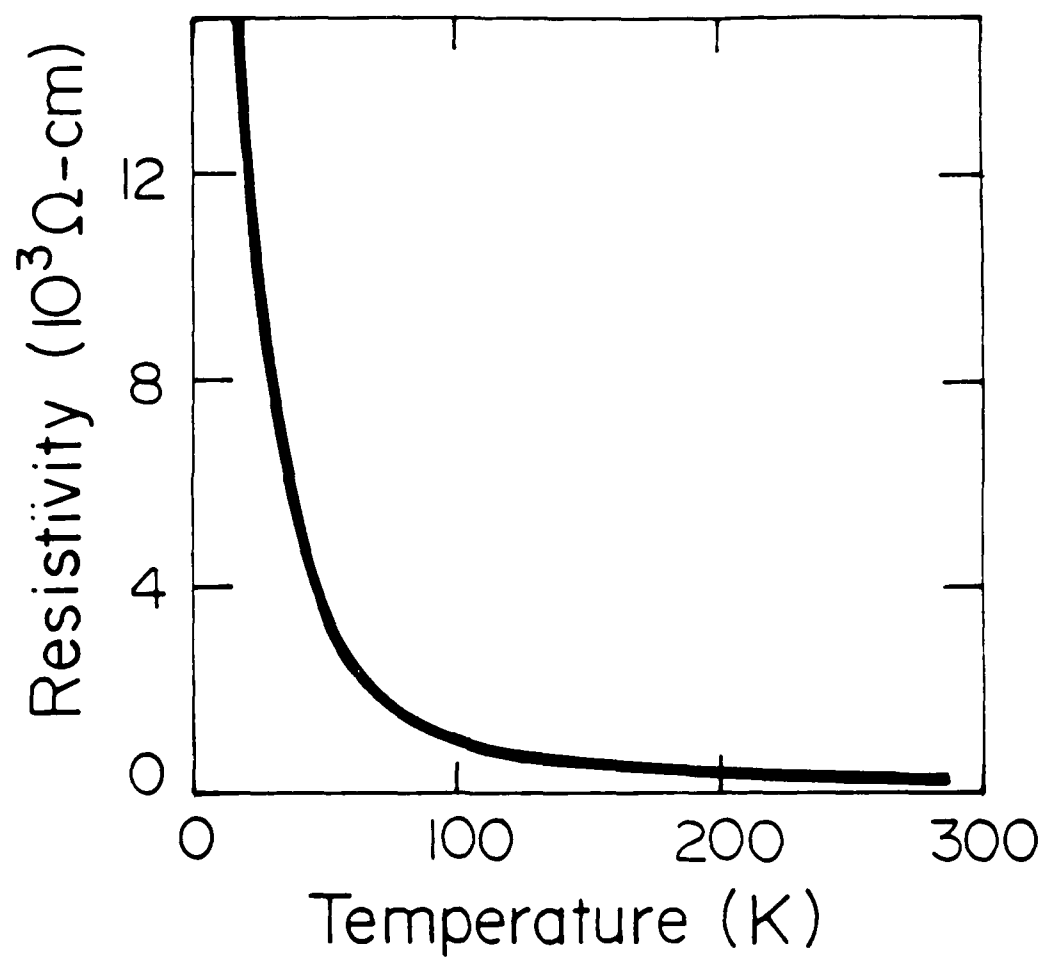
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